A novel strategy to prepare Sb thin film sandwiched between the reduced graphene oxide and Ni foam as binder-free anode material for lithium-ion batteries

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Abstract

A simple and inexpensive route is developed to synthesis the Sb thin film sandwiched between the reduced graphene oxide and the Ni foam (RGO-Sb_{TF}-Ni) by a galvanic replacement reaction along with a pulse electrophoretic deposition route. As a binder-free anode material for lithium ion batteries, the RGO-Sb_{TF}-Ni exhibits a high initial discharge capacity of 872.9 mAh g⁻¹ and an enhanced coulombic efficiency of 66.0% at a current density of 100 mA g⁻¹ in the first cycle. In addition, a substantial discharge capacity of 424.1 mAh g⁻¹ can be retained even after 50 repeated cycles. The enhanced performances of the designed binder-free anode material can be attributed to the novel hierarchical sandwich laminated structure with an excellent electrical contact, and the synergistic effect between the Sb thin film with high specific capacity and flexible RGO with good buffer effect to alleviate the strain caused by the large volume change.

Keywords: Lithium-ion batteries; Anode; Sb; Reduced graphene oxide; Thin film

1. Introduction

The slurry-casting process is a conventional method to fabricate the working anode for lithium ion batteries (LIBs). Normally, the working electrode is prepared by mixing the active materials, conductive carbon black and polyvinylidene fluoride (PVDF) with an approximate weight ratio. Then the N-methyl-2-pyrrolidone is added to the mixture to form homogeneous slurry and subsequently pressed onto Cu foil [1, 2]. In recent years, the thin film materials have been developed revolutionarily

as new type of binder-free anode materials for LIBs [3]. Compared with the conventional ones, the thin film materials have many special advantages. Firstly, the active materials are directly fabricated onto the current collector without a binder, which can avoid using a binder affecting the enhancement of the specific capacity because of the extra inactive materials. What's more, one-step fabrication method without slurry-casting process can short processing time. Furthermore, the saving of retreatment process can prevent active materials from aggregating to form large particles during the mixing process. In addition, this method is inexpensive and industrially scalable.

Many binder-free methods are invented to prepare thin film materials. The electrochemical deposition of active materials on two or three dimensional substrates has been confirmed as the most common and promising route to enhance the cycling performance of electrodes. This enhancement is mainly due to the good electrical contact between the active material and the current collector, as well as the ability to buffer volume changes during the lithium insertion process [4]. The electrochemical deposition method has been successfully applied to prepare thin film alloy materials like Sn-Ni [5-7], Sn-Cu [8-9], Sn-Co [10], Sn-Sb [11], Sn-Sb-Co [12], pure Sn [13], and so on. Electron-beam deposition technology has also been developed to fabricate thin film materials, for instance, Cu-Sn composite thin film, Ni_3Sn_2 thin film and Al-Sn alloy thin films, which have been successfully prepared using this route by M. Zhu [14], Sung-Man Lee [15] and Min Zhu [16], respectively. In addition, gas deposition [17], electrophoretic deposition [18] and radio frequency magnetron sputtering [19, 20] have also been employed to fabricate thin film electrodes. All thin film materials mentioned above have exhibited enhanced electrochemical performances in LIBs.

Although there is a considerable success in synthesis of thin film materials for LIBs, the electroless plate route based on binder-free galvanic replacement reaction has never been developed in this field, especially for antimony (Sb) thin film electrode. In this work, we report a successful synthesis method to fabricate Sb thin film onto nickel (Ni) foam ($\text{Sb}_{\text{TF}}\text{-Ni}$). Our route is using Ni foam as a template and a reducing agent for the replacement reaction from Sb^{3+} to Sb, and then as a substrate for deposition of the Sb thin film. To further improve the cycling performance of $\text{Sb}_{\text{TF}}\text{-Ni}$, the reduced graphene oxide (RGO) thin film is deposited onto the surface of $\text{Sb}_{\text{TF}}\text{-Ni}$ by a facile pulsed electrophoretic deposition route. Because the Sb thin film is skillfully sandwiched between the Ni foam current collector and high conductive/flexible RGO ($\text{RGO-Sb}_{\text{TF}}\text{-Ni}$), the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ has cooperative advantages in electrical

conductivity and buffer effect to retard the volume changes during lithium insertion process. Our results demonstrate that the RGO-Sb_{TF}-Ni has better electrochemical performances. We think this work may enrich the methods to fabricate thin film materials and motivate further exploration for preparation other metal-RGO thin film composites for LIBs.

2. Experimental

2.1 Preparation of Sb_{TF}-Ni and RGO-Sb_{TF}-Ni

All reagents were purchased from Aladdin Reagent Co., Ltd. (China). The Sb_{TF}-Ni was fabricated by a facile galvanic replacement reaction route. In a typical synthesis process, 1.14 g antimony trichloride was well-dispersed in 35 mL glycerinum solvent by ultrasonication and magnetic stirring. And then the mixture was transferred to a 50 mL Teflon-lined autoclave. After the cleaned Ni foam being immersed into the mixture, the autoclave was tightly sealed and maintained at 100 °C for 12 h. When cooled naturally to room temperature, the as-prepared products were washed thoroughly by absolute ethyl alcohol, and then dried in a vacuum oven at 60 °C overnight. To fabricate the RGO-Sb_{TF}-Ni, a pulsed electrophoretic deposition route was used. Graphene oxide (GO) was prepared by a modified Hummer's method [21]. Then 50 mg GO was well dissolved in 100 mL distilled water under ultrasonication for 30 min to form a colloidal precursor solution. The as-prepared Sb_{TF}-Ni and pure Ni foam were used as the negative electrode and the positive electrode, respectively. The distance of the negative and positive electrodes was 10 mm. An applied potential of 5 V was used for 30 s two times with an interval time of 1 min to the electrophoretic deposit. Subsequently, the obtained RGO-Sb_{TF}-Ni was washed thoroughly by distilled water and dried at 60 °C under vacuum.

2.2 Materials Characterization

The phase purity and the structure of the as-prepared products were determined by powder X-ray diffractometer (XRD, Bruker Corporation, Germany) with copper target at a scan rate of 4 °/min. The Sb contents in Sb_{TF}-Ni were determined by inductively coupled plasma spectrometry (ICP). Thermogravimetric analysis (TGA) was performed in air from room temperature to 900 °C with a heating rate of 5 °C min⁻¹ by using an STA 449 Jupiter (NETZSCH) thermogravimetry analyzer. X-ray photoelectron spectrometry (XPS) spectra with an ESCALABMKLL X-ray photoelectron spectrometer

using an aluminum target source was employed to evaluate the chemical status of the samples. The morphologies, energy-dispersive X-ray spectroscopy (EDS) element mapping of the products were characterized by scanning electron microscope (SEM, HITACHI S-4800, Japan) at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV.

2.3 Electrochemical measurements

For electrochemical tests, the $\text{Sb}_{\text{TF}}\text{-Ni}$ and $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ were directly used as the working electrode. The cells were assembled in a glove box filled with highly pure argon gas. The electrochemical measurements were carried out by using CR 2025 coin-type cells with pure lithium as the counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate (1:1 in volume) as the electrolyte. The cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted on a BioLogic VMP3 electrochemical workstation. The charge-discharge performance was tested between 0.01 V and 2.0 V using a programmable battery testing system (LAND CT2001A) at room temperature.

3. Results and discussion

The strategy for synthesizing $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ is schematically depicted in Fig. 1. Firstly, the Sb thin film is deposited onto the Ni foam by a facile galvanic replacement reaction route. Here the Ni foam is a reducing agent for the replacement reaction from Sb^{3+} to Sb while the Ni to Ni^{2+} , and then as substrate for deposition of Sb thin film. Secondly, the RGO thin film is deposited onto the surface of $\text{Sb}_{\text{TF}}\text{-Ni}$ by a facile pulsed electrophoretic deposition route. Our design is to acquire a sandwich laminated $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$, in which the Sb thin film is skillfully sandwiched between the Ni foam current collector and high conductive/flexible RGO. This design is aimed at obtaining the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ composite has cooperative advantages: (1) excellent electrical contact between the Sb thin film active material and the current collector as well as the RGO thin film; (2) good buffer effect to release mechanical stress generated by volume changes during lithium insertion process. Based on these advantages, the electrochemical cycling performance of the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ anode is attempted to improve for LIBs.

Fig. 2a is the XRD patterns of the $\text{Sb}_{\text{TF}}\text{-Ni}$ and $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$. As shown in Fig. 2a, the peaks at

23.69°, 25.15°, 28.69°, 40.08°, 41.95°, 47.07°, 48.43°, 51.59° and 59.39° can be indexed to Sb phase, corresponding to the reference Sb spectrum (JCPDS 35-0732). It can be seen that all diffraction peaks of Sb_{TF}-Ni and RGO-Sb_{TF}-Ni agree well with the peaks of the Sb, indicating the pure phase of Sb thin film onto Ni foam. Furthermore, in the RGO-Sb_{TF}-Ni, a broad peak appeared at diffraction angles of about 20°~25° is ascribed to the RGO crystal plane. The peaks of Sb thin film and RGO coexist in the XRD, suggesting the coexistence of RGO thin film and Sb thin film in the RGO-Sb_{TF}-Ni. In addition, the Sb contents in Sb_{TF}-Ni are calculated according to the calculation process (Section 1, Supplementary Materials) and determined by ICP. Both imply that the weight percentage of Sb in Sb_{TF}-Ni is 6.35 wt. %.

To determine the actual content of RGO in the RGO-Sb_{TF}-Ni, the thermogravimetry analysis is carried out. As shown in Fig.2b, the approximate proportion of RGO is evaluated to be 2.5 wt. % (the detailed calculation process see Section 1, Supplementary Materials) in the RGO-Sb_{TF}-Ni. Together with the contents of Sb and RGO, it can be seen that there are about 28.76 wt. % of RGO and 71.24 wt. % of Sb in the RGO-Sb_{TF}-Ni. Furthermore, the main weight loss in the RGO-Sb_{TF}-Ni is at the temperature range of 500~570 °C, which corresponds to the oxidation of the RGO into CO₂ and H₂O. And there is no obviously weight loss at approximately 330 °C, which indicates the majority of GO have been reduced to the RGO in the pulsed electrophoretic deposition process [22].

The XPS spectrum is used to measure chemical composition of RGO-Sb_{TF}-Ni. As shown in Fig. 3a, the peaks of Sb 3d, Sb 4d and C 1 s are distinctly observed in the survey scan spectrum, indicating the co-existence of Sb and C elements in the RGO-Sb_{TF}-Ni. For Fig. 3b, the C 1s spectra mainly present two peaks corresponding to carbon atoms bonding with different oxygenated functional groups. The peaks at the binding energy of 284.5 eV and 285.8 eV are point to the C-C and C-O, respectively, while the peaks of other oxygenated functional C=O and O-C=O groups are slight. According to their intensity ratios, the results suggest that the number of oxygenated functional groups is largely reduced during the pulsed electrophoretic deposition process in the RGO-Sb_{TF}-Ni. In the Sb 3d spectrum, two peaks at 530.8 eV and 540.3 eV are attributed to Sb 3d_{5/2} and Sb 3d_{3/2}, respectively. Note that the peaks of Ni do not obviously exist in the survey scan spectrum, suggesting that the Sb thin film is completely covered onto the Ni foam.

To investigate the surface images of pure Ni foam, Sb_{TF}-Ni and RGO-Sb_{TF}-Ni, the representative

SEM images are presented in Fig. 4a-c. As depicted in Fig. 4a, smooth surface of the Ni foam can be seen before deposition of Sb and RGO. The inset of Fig. 4a shows that the Ni foam exhibits a three-dimensional (3D) porous structure. Fig. 4b presents a high-magnification SEM image of Sb thin film deposited onto the Ni foam surface. It can be seen that some Sb particles with sizes of hundreds of nanometers are located onto the surface of Ni foam during the galvanic replacement reaction process. The low-magnification SEM image of Sb_{TF}-Ni is shown in the inset of Fig. 4b, which exhibits that the Sb thin film is uniformly coated on the 3D porous Ni foam. From the Fig. 4c, we observe that the RGO is well coated on the Sb_{TF}-Ni in the pulsed electrophoretic deposition process, indicating the successful formation of a RGO-Sb_{TF}-Ni composite alliance. To check whether the Sb has a good contact with RGO, the TEM and HRTEM images of RGO-Sb_{TF}-Ni are performed as shown in Fig. 4d and 4e, respectively. Obviously, the TEM and HRTEM pictures testify that the Sb has a good contact with RGO. To further analyze the distribution of the Ni, Sb and C in the RGO-Sb_{TF}-Ni, elemental mapping is carried out. As shown in Fig. 4f, all the energy-filtered SEM maps of the Ni, Sb and C match well with the SEM image, indicating that the Ni, Sb and RGO are uniform dispersion and coexistence over the whole composite.

To find the process progresses of deposition of Sb film onto Ni foam via replacement reaction, the Sb film fabricated at different times are compared. As shown in Fig. S1 (Supplementary Materials), the weight (in per electrode, 1.13 cm²) of Sb film at different preparation times 4 h, 8 h, 12 h and 16 h are 2.35, 2.94, 3.18 and 3.28 mg, respectively. Moreover, the corresponding thicknesses of the Sb film are 3.56, 4.34, 4.85 and 5.05 μ m, respectively, which are measured by the SEM images (Fig. S2, Supplementary Materials). Furthermore, the contents of Sb film increases fleetly within deposition times of 8 h and then slowly reaches the saturation point around 16 h. When the deposition time is more than 16 h, the composed particles of deposited film aggregate and become extremely large (Fig. S3), hence the deposition time should be limited within 16 h. To detect the influence of film thickness on electrochemical properties, the lithium storage properties of Sb films with different duration times are exhibited in Fig. S4 (Supplementary Materials). With increasing of the thickness of Sb film, the contents of Sb film increase and thus leading to enhanced discharge capacities. The sample fabricated at 16 h has the highest discharge capacity, but it fades fast compared with other ones. This can be attributed to the following factors: (1) the deposited film of Sb particles will be aggregated and become larger with the increase of replacement reaction time; (2) the thicker Sb thin film materials are

fabricated, the easier they fall down from the supported Ni foam during the repeated cycles. Took into comparison the electrochemical properties of the Sb films fabricated at different times, it can be seen that the sample fabricated at 12 h has better integrated performances between discharge capacities and cycling stability. Therefore, we choose this one to enhance the electrochemical properties as anode material for LIBs.

Apart from the Ni foam, the flat Ni foil is also introduced to fabricate the Sb thin film by the similarly methods. Analogously, the flat Ni foil is not only served as a current collector, but also acted as a reducing agent for the replacement reaction from Sb^{3+} to Sb. The SEM image of Sb film deposited onto flat Ni is shown in Fig. S6, which exhibits that there is no obvious difference of the Sb film deposited between the Ni foam and the flat Ni foil. Fig. S7 exhibits that the Sb film deposited onto flat Ni at deposition times of 12 h has lower discharge capacity in comparison with the sample deposited onto Ni foam in the same condition. This can be ascribed to the factor that the Ni foam has larger specific surface area to increase the opportunity to occur replacement reaction between the Ni and Sb^{3+} and thus increasing the actual contents of Sb film as well as the derived discharge capacity.

The CV curves of first three cycles of the RGO-Sb_{TF}-Ni anode at a scan rate of 0.1 mV s⁻¹ are presented in Fig. 5a. In the first cathodic sweep, a cathodic peak around 0.6 V is ascribed to the lithiation of Sb at the beginning and the subsequent decomposition of the electrolyte to form solid electrolyte interphase (SEI) film, which is in according with the report by H.L. Lv [23]. It doesn't appear in the second cycle, reflecting the stable property of SEI film in the first cycle. This cathodic peak is replaced by the peak located at 0.77 V in following cycles, which is attributed to the reaction of metallic Sb to alloyed Li₃Sb. [24] During the anodic process, the peak located at about 1.15 V corresponds to delithiation reactions of Li₃Sb to Sb. Apart from the first cycle, all peaks are stable and reversible in the following cycles, implying the good electrochemical reversibility of RGO-Sb_{TF}-Ni during cycling. Based on the analysis above, the electrochemical process for the RGO-Sb_{TF}-Ni is expected to evolve by a reversible electrochemical process as follows: [25, 26]

Fig. 5b and 5c show the initial two charge and discharge curves of the Sb_{TF}-Ni and RGO-Sb_{TF}-Ni measured between 0.01 and 2.0 V at a current density of 100 mA g⁻¹, respectively. For the insertion with lithium, the first discharge is characterized by a wide flat plateau near 0.80 V, corresponding the

reaction of metallic Sb to alloyed Li_3Sb . During lithium exsertion process, the delithiation reaction from Li_3Sb to Sb is represented by one plateau around 1.05 V. The voltage plateaus in the discharge and charge curves (Fig. 5b-c) agree well with the cathodic and anodic peaks in the CV curves (Fig. 5a), respectively. In addition, the discharge voltage plateaus of the $\text{Sb}_{\text{TF}}\text{-Ni}$ is slightly lower than while the charge voltage plateaus is higher than that of $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$. This may be attributed to the fact that the RGO in the composite can enhance electrical conductivity, lower the impedance of the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$, and thus enhancing its discharge voltage plateaus and decreasing its charge voltage plateaus.

The cycling behaviors of $\text{Sb}_{\text{TF}}\text{-Ni}$ and $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ electrodes are shown in Fig. 5d and 5e, respectively. As shown in Fig. 5d, the $\text{Sb}_{\text{TF}}\text{-Ni}$ can deliver a specific discharge capacity of 1177 mAh g^{-1} and a specific charge capacity of 620.8 mAh g^{-1} with a coulombic efficiency of 52.7% in the initial cycle. The discharge capacity remains 558.8 mAh g^{-1} after 1 cycle and 189.1 mAh g^{-1} after 50 cycles. On the contrary, as for $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ (Fig. 5e), a specific capacity of 872.9 mAh g^{-1} and 576.1 mAh g^{-1} is delivered by the first discharge and charge step with a coulombic efficiency of 66.0%. Though the second discharge capacity decays to 650.8 mAh g^{-1} , the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ anode shows a stable cycling performance after the first cycle. A high reversible discharge capacity of 424.1 mAh g^{-1} is retained even after 50 cycles. The cycling performance of RGO alone deposited on Ni foam is shown in Fig. S5 (Supplementary Materials), which exhibits that the RGO has long cycling stability but low capacity, indicating the specific capacity of $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ delivered mainly by the Sb film instead of the RGO. Compared with the $\text{Sb}_{\text{TF}}\text{-Ni}$, the improved coulombic efficiency of $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ can be attributed to the decreased formation of solid electrolyte interphase (SEI) layer on the electrode surface during the first discharge step because of coated with RGO which decreases the contact area between active materials and the electrolyte [27]. The enhanced cycling performance of $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ is owing to the promising and flexible RGO thin film tightly coated onto the Sb thin film, which has good buffer effect to release mechanical stress generated by volume changes during lithiation/delithiation process.

The high rate discharge abilities of $\text{Sb}_{\text{TF}}\text{-Ni}$ (Fig. 4f) and $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ (Fig. 4g) electrode are investigated at various current densities ranging from 100 to 1000 mA g^{-1} . Obviously, the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ electrode shows a more decent rate capability compared with the $\text{Sb}_{\text{TF}}\text{-Ni}$. For the $\text{RGO-Sb}_{\text{TF}}\text{-Ni}$ composite, average discharge capacities of 557.2, 455.2, 298.2 and 158.0 mAh g^{-1} can be delivered at 100, 200, 500 and 1000 mA g^{-1} , separately. Moreover, when the current density goes back to 100 mA g^{-1} , the specific discharge capacity can return to 418.3 mAh g^{-1} and maintain at the value of

414.8 mAh g⁻¹ after 50 cycles. These results indicate the electrode is stable and have high reversibility.

EIS measurements of Sb_{TF}-Ni and RGO-Sb_{TF}-Ni have been conducted and fitted by using equivalent circuit (Fig. 5h) to evaluate the resistance against charge and ion transfer during cycles. Obviously, The RGO-Sb_{TF}-Ni exhibits decreased charge transfer resistance (R_{ct} = 200.7 Ω), which is lower than that of Sb_{TF}-Ni (R_{ct} = 307.4 Ω). This result indicates that the RGO matrix can provides a highly conductive network [28] to boost the electronic conductivity, promote the electronic transport and electrons and enable much easier charge transfer on the electrode/electrolyte interface. Thus, the improved electronic conductivity by the promising RGO is considered to be a key factor to result in a low resistant and enhance the electrochemical performance of RGO-Sb_{TF}-Ni.

To further investigate the morphology and structure variation of the de-lithiated Sb_{TF}-Ni and RGO-Sb_{TF}-Ni electrodes, SEM images of two samples after 50 charge–discharge cycles are carried out. As revealed in Fig. 6a and 6b, some of the Sb thin film are cracked and fallen down from the Ni foam substrate, and thus resulting in loss of electrical contact between Sb particles and current collector, leading to decrease of active materials and rapid capacity fading. Nevertheless, there are no obvious detachments of RGO-Sb film from current collector, which can be attributed to the protective effect of the RGO coated onto the Sb thin film to form a sandwich laminated RGO-Sb_{TF}-Ni composite. This can be the main factor to enhance the cycling performance of RGO-Sb_{TF}-Ni.

On the basis of the above results, the enhanced electrochemical performance of the RGO-Sb_{TF}-Ni composite can be attributed to the advantage of hierarchical sandwich laminated composite and the synergistic effect between Sb thin film and the RGO. Detailedly: (1) the Sb thin film which covers onto the 3D conductive Ni foam substrate as well as coated with conductive RGO has a advantage to improve electrochemical performance due to the good electrical contact between the active material and the current collector as well as the RGO; (2) the hierarchical sandwich laminated structure can contribute its ability to buffer huge volume expansion during cycling; (3) the RGO, tightly coated onto the Sb thin film, acts as the protector to prevent the Sb thin film from falling down from the Ni foam substrate and thus enhancing the cycling performance of RGO-Sb_{TF}-Ni.

4. Conclusions

In summary, a novel RGO-Sb composite thin film has been successfully fabricated on Ni foam by

the binder-free galvanic replacement reaction and pulse electrophoretic deposition technique. The Sb thin film, which has deposited onto the Ni foam, is further tightly coated with the RGO to form a novel hierarchical sandwich laminated composite. Based on its structural advantage, the RGO-Sb_{TF}-Ni exhibits improved lithium storage performance in terms of resistance, cycling stability and rate discharge ability in comparison with the Sb_{TF}-Ni. The significant electrochemical performance is mainly attributed to the good electrical conductivity and protection effect of RGO. Based on the advantages of preparation methods and excellent electrochemical performances, the RGO-Sb_{TF}-Ni is considered as one of promising candidate anode materials for future LIBs. Our work presents a facile strategy to fabricate the hierarchical sandwich laminated thin film composite, which can motivate further exploration for preparation other metal-RGO thin film composites in the field of energy storage and electrical devices.

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Supplementary Materials

Supplementary data associated with this article can be found, in the online version, at <http://xxx...>

References

- [1] Y.H. Xu, Q. Liu, Y.J. Zhu, Y.H. Liu, A. Langrock, M.R. Zachariah, C.S. Wang, Uniform Nano-Sn/C Composite Anodes for Lithium Ion Batteries, *Nano letters*, 13 (2013) 470-474.
- [2] Q. Cheng, R. Yuge, K. Nakahara, N. Tamura, S. Miyamoto, KOH etched graphite for fast chargeable lithium-ion batteries, *Journal of Power Sources*, 284 (2015) 258-263.
- [3] Y. Yang, D.Q. Chen, B. Liu, J.B. Zhao, Binder-Free Si Nanoparticle Electrode with 3D Porous Structure Prepared by Electrophoretic Deposition for Lithium-Ion Batteries, *ACS applied materials & interfaces*, 7 (2015) 7497-7504.
- [4] F. Nacimiento, R. Alcantara, J.R. Gonzalez, J.L. Tirado, Electrodeposited Polyacrylonitrile and Cobalt-Tin Composite Thin Film on Titanium Substrate, *Journal of the Electrochemical Society*, 159 (2012) A1028-A1033.
- [5] J. Hassoun, S. Panero, P. Simon, P.L. Taberna, B. Scrosati, High-rate, long-life Ni-Sn

nanostructured electrodes for lithium-ion batteries, *Adv Mater*, 19 (2007) 1632-1635.

[6] H. Mukaibo, T. Sumi, T. Yokoshima, T. Momma, T. Osaka, Electrodeposited Sn-Ni alloy film as a high capacity anode material for lithium-ion secondary batteries, *Electrochim Solid St*, 6 (2003) A218-A220.

[7] J. Hassoun, S. Panero, B. Scrosati, Electrodeposited Ni-Sn intermetallic electrodes for advanced lithium ion batteries, *Journal of Power Sources*, 160 (2006) 1336-1341.

[8] H.C. Shin, M.L. Liu, Three-dimensional porous copper-tin alloy electrodes for rechargeable lithium batteries, *Adv Funct Mater*, 15 (2005) 582-586.

[9] F.S. Ke, L. Huang, J.S. Cai, S.G. Sun, Electroplating synthesis and electrochemical properties of macroporous Sn-Cu alloy electrode for lithium-ion batteries, *Electrochimica Acta*, 52 (2007) 6741-6747.

[10] C.G. Yang, D.W. Zhang, Y.B. Zhao, Y.H. Lu, L. Wang, J.B. Goodenough, Nickel foam supported Sn-Co alloy film as anode for lithium ion batteries, *Journal of Power Sources*, 196 (2011) 10673-10678.

[11] S.Q. Zhang, C.H. Chen, The synthesis of composite Sn-SnSb films for lithium-ion batteries by electrochemical deposition, *Mater Res Bull*, 43 (2008) 3601-3606.

[12] T. Tabuchi, N. Hochgatterer, Z. Ogumi, M. Winter, Ternary Sn-Sb-Co alloy film as new negative electrode for lithium-ion cells, *Journal of Power Sources*, 188 (2009) 552-557.

[13] D.H. Nam, R.H. Kim, D.W. Han, H.S. Kwon, Electrochemical performances of Sn anode electrodeposited on porous Cu foam for Li-ion batteries, *Electrochimica Acta*, 66 (2012) 126-132.

[14] R.Z. Hu, M.Q. Zeng, M. Zhu, Cyclic durable high-capacity Sn/Cu₆Sn₅ composite thin film anodes for lithium ion batteries prepared by electron-beam evaporation deposition, *Electrochimica Acta*, 54 (2009) 2843-2850.

[15] Y.L. Kim, H.Y. Lee, S.W. Jang, S.J. Lee, H.K. Baik, Y.S. Yoon, Y.S. Park, S.M. Lee, Nanostructured Ni₃Sn₂ thin film as anodes for thin film rechargeable lithium batteries, *Solid State Ionics*, 160 (2003) 235-240.

[16] R.Z. Hu, M.Q. Zeng, C.Y.V. Li, M. Zhu, Microstructure and electrochemical performance of thin film anodes for lithium ion batteries in immiscible Al-Sn system, *J Power Sources*, 188 (2009) 268-273.

[17] H. Usui, M. Nomura, H. Nishino, M. Kusatsu, T. Murota, H. Sakaguchi, Gadolinium silicide/silicon composite with excellent high-rate performance as lithium-ion battery anode, *Materials Letters*, 130 (2014) 61-64.

[18] K. Ui, S. Kawamura, N. Kumagai, Fabrication of binder-free SnO₂ nanoparticle electrode for lithium secondary batteries by electrophoretic deposition method, *Electrochimica Acta*, 76 (2012) 383-388.

[19] Y. Yu, C. Yue, S. Sun, W. Lin, H. Su, B. Xu, J. Li, S. Wu, J. Li, J. Kang, The effects of different core-shell structures on the electrochemical performances of Si-Ge nanorod arrays as anodes for micro-lithium ion batteries, *ACS applied materials & interfaces*, 6 (2014) 5884-5890.

[20] R.Z. Hu, M. Zhu, H. Wang, J.W. Liu, L.Z. Ouyang, J. Zou, Sn buffered by shape memory effect of NiTi alloys as high-performance anodes for lithium ion batteries, *Acta Mater*, 60 (2012) 4695-4703.

[21] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *J Am Chem Soc*, 80 (1958) 1339-1339.

- [22] W. Jiang, F. Liang, J.W. Wang, L. Su, Y.M. Wu, L.M. Wang, Enhanced electrochemical performances of FeOx-graphene nanocomposites as anode materials for alkaline nickel-iron batteries, *Rsc Adv*, 4 (2014) 15394-15399.
- [23] H.L. Lv, S. Qiu, G.X. Lu, Y. Fu, X.Y. Li, C.X. Hu, J.R. Liu, Nanostructured Antimony/carbon Composite Fibers as Anode Material for Lithium-ion Battery, *Electrochimica Acta*, 151 (2015) 214-221.
- [24] A. Dailly, J. Ghanbaja, P. Willmann, D. Billaud, Lithium insertion into new graphite-antimony composites, *Electrochimica Acta*, 48 (2003) 977-984.
- [25] D.H. Chang, H. Huo, K.E. Johnston, M. Menetrier, L. Monconduit, C.P. Grey, A. Van der Ven, Elucidating the origins of phase transformation hysteresis during electrochemical cycling of Li-Sb electrodes, *J Mater Chem A*, 3 (2015) 18928-18943.
- [26] L. Fan, J.J. Zhang, J.H. Cui, Y.C. Zhu, J.W. Liang, L.L. Wang, Y.T. Qian, Electrochemical performance of rod-like Sb-C composite as anodes for Li-ion and Na-ion batteries, *J Mater Chem A*, 3 (2015) 3276-3280.
- [27] N. Liu, Z.D. Lu, J. Zhao, M.T. McDowell, H.W. Lee, W.T. Zhao, Y. Cui, A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes, *Nat Nanotechnol*, 9 (2014) 187-192.
- [28] Z.L. Wang, D. Xu, Y. Huang, Z. Wu, L.M. Wang, X.B. Zhang, Facile, mild and fast thermal-decomposition reduction of graphene oxide in air and its application in high-performance lithium batteries, *Chem Commun*, 48 (2012) 976-978.

Figure Captions

Fig. 1. Schematic illustration of the synthesis route for RGO-Sb_{TF}-Ni.

Fig. 2. (a) XRD patterns, (b) TG curves of bare Sb_{TF}-Ni and RGO-Sb_{TF}-Ni.

Fig. 3. XPS spectra of RGO-Sb_{TF}-Ni, (a) survey scan, (b) C 1 s, (c) Sb 3 d.

Fig. 4. SEM images of (a) pure Ni foam, (b) Sb_{TF}-Ni and (c) RGO-Sb_{TF}-Ni, (d) TEM and (e) HRTEM images of RGO-Sb_{TF}-Ni and (f) SEM image and element mappings of the RGO-Sb_{TF}-Ni.

Fig. 5. (a) CV curves of RGO-Sb_{TF}-Ni; Voltage-Capacity curves of (b) Sb_{TF}-Ni and (c) RGO-Sb_{TF}-Ni; galvanostatic discharge-charge cycles performances of (d) Sb_{TF}-Ni and (e) RGO-Sb_{TF}-Ni; rate charge-discharge performances of (f) Sb_{TF}-Ni and (g) RGO-Sb_{TF}-Ni and (h) EIS measurements of Sb_{TF}-Ni and RGO-Sb_{TF}-Ni.

Fig. 6. SEM images of (a, b) Sb_{TF}-Ni and (c, d) RGO-Sb_{TF}-Ni after 50 cycles.

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